Probe Size Dependent Rotational Dynamics in Polymer by Single Molecule Spectroscopy

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1. Introduction

A drastic slowdown of the dynamics of a liquid close to its glass transition temperature is observed in many different materials ranging from simple molecular glass formers to complex synthetic polymers. The non-exponential relaxation dynamics and non-Arrhenius type of temperature dependence of mean relaxation times has been observed by many ensemble techniques such as EPR, NMR and dielectric spectroscopy and recently by single molecule spectroscopy. Most of these studies attributed this anomalous behaviour compared to ordinary liquid to the presence of heterogeneity in the systems. Single molecule techniques are able to distinguish the dynamical change of a physical property over space as well as over time, which are referred to as spatial heterogeneity and dynamical heterogeneity, respectively. In literature, there are very few probe size dependent studies and even only one single molecule study by Mackowiak et al. [1]. Using different probe molecules Cierone et al. [1] have calculated the length scale on which the system becomes homogeneous for simple molecular liquid OTP from the trend of change in ß value with change in probe size. Mackowiak et al. [2] have studied rotational dynamics for different perylene dimide molecules in simple molecular glass former glycerol and found that the change in distribution width of rotational times cannot be explained by spatial averaging but by temporal averaging, which indicates the presence of dynamical heterogeneity in glycerol.

We study the rotational dynamics of four different perylene dimide molecules in polymer poly(methylacrylate) (PMA) and poly(vinylacetate) (PVAc) close to the glass transition temperature. Two of them are rigid molecules and the two other ones are flexible molecules. The temperature dependence of mean relaxation times for all the molecules is similar in both polymers, and, most importantly, they follow the Debye-Stokes-Einstein (DSE) law for polymer viscosity. For PMA it is exactly same as the DSE prediction and for PVAc it is 5 times faster than the DSE prediction. For flexible molecules the rotational dynamics are faster than for rigid molecules, and only the rigid part of the molecules plays a role in the rotational dynamics. The change in distribution width of rotational times and stretching exponents cannot be explained as Cierone et al. [1] or Mackowial et al. [2] suggested, but we explain it by changes in dynamical heterogeneity time scale.

2. Results and discussion

We study rotational dynamics of two rigid molecules PDI1 ((N,N'-Bis(2,6-dimethylphenyl)perylene-3,4,9,10-tetracarboxylic dimide) and PDI3 (N,N'-Bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylenedicarboximide) and two flexible molecules PDI2

(N,N'-bis(1-hexylheptyl)-perylene-3,4:9,10-bis-(dicarboximide)) and PDI13 (N,N'-Ditridecylperylene-3,4,9,10-tetracarboxylic dimide) in PMA, and only PDI1 and PDI2 in PVAc. The hydrodynamic volumes calculated using the DSE law for rigid molecules are nearly the same as the ones calculated from fluorescence correlation spectroscopy (FCS) measurements in dodecane, but for flexible molecules the hydrodynamic volumes are nearly the same as the ones calculated from the van der Waals volume of the rigid part of the molecules. For flexible molecules the flexible side chains make some conformational change so that the only rigid part of the molecules takes part in the rotational dynamics. The faster dynamics of PDI2 compared to PDI1 are also observed by steady state anisotropy measurements; the same rate increase in dynamics is measured as in single molecule spectroscopy. We have extended SM measurements for binary mixtures of PDI1 and PDI2, and observed that the distribution of rotational dynamics shifts to higher rotational times if we increase the concentration of PDI1. This implies slower dynamics of PDI1 compared to PDI2.

The mean stretching exponents (β) are almost the same for all molecules. The change in distribution width of rotational times (σ_τ) for all molecules have a similar trend for the stretching exponents (σ_β): PDI3 > PDI ~ PDI13 > PDI2. This trend cannot be explained by spatial averaging as Cierone et al. [1] explained and also not by temporal averaging as Mackowiak et al. [2] explained. We have explained all the experimental findings for rotational dynamics of PDI1 in PMA by using a simple model of dynamical heterogeneity based on a Gaussian distribution of activation energies in a VFTH (Voge l–Fulcher – Tammann - Hasse) type temperature dependence of polymer viscosity. Nearly the same value of mean β values and a similar change in σ_τ and σ_β can be explained by changes in dynamical heterogeneity time scale (τ_{dh}) using a dynamical heterogeneity model. For rigid molecules the trend of change in τ_{dh} is PDI3 > PDI1, corresponding to the trend in molecular size, and for flexible molecules it is similar – PDI13 > PDI2. τ_{dh} for PDI1 and PDI13 is the same, despite the difference in molecular size. The trend of mean rotational times for the molecules is PDI3 > PDI1 > PDI2 ~ PDI13, similar to the trend of τ_{dh} for the molecules except PDI13. τ_{dh} for PDI13 is expected to be larger than for PDI1, because of its larger size, but it could also be smaller, as the mean rotational time for PDI13 is shorter than for PDI1. These two factors have opposite effects, and so, τ_{dh} for PDI13 is nearly the same as for PDI1.

3. Conclusion

The rotational dynamics of probe molecules follow the DSE law for polymer viscosity. The rotational dynamics of flexible molecules are faster than of rigid molecules, as only the rigid part of flexible molecules takes part in the rotational dynamics. The change in distribution width of rotational times and stretching exponents can be explained by a change in τ_{dh} for all the molecules, and τ_{dh} depends on both molecular size and mean rotational time of the probe molecules.

References

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